(19) Europäisches Pat ntamt
European Pat nt Offic
Office européen des brevets

(11) EP 0 682 678 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
09.12.1998 Bulletin 1998/50

(51) Int Cl.6: C08J 5/18, B29D 7/01, C08L 23/08 // B29K9:06, B29K23:00

(21) Application number: 94907999.0

(22) Date of filing: 03.02.1994

(86) International application number:
PCT/US94/01376

(87) International publication number:
WO 94/18263 (18.08.1994 Gazette 1994/19)

(54) THERMOPLASTIC ELASTOMER COPOLYMER FILMS

FOLIEN AUS THERMOPLASTISCHEN ELASTOMER-KOPOLYMEREN

FILMS COPOLYMERES ELASTOMERES THERMOPLASTIQUES

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL PT SE

(30) Priority: 03.02.1993 US 13518

(43) Date of publication of application:
22.11.1995 Bulletin 1995/47

(73) Proprietor: EXXON CHEMICAL PATENTS INC.
Baytown, TX 77520-2149 (US)

(72) Inventors:
- ERDERLY, Thomas, Craig
Baytown, TX 77521 (US)
- MACKAY, John, Hugh, III
Crystal Lake, IL 60014 (US)
- NARRAMORE, Russell, Harrell
Kingwood, Texas 77345 (US)

(74) Representative: Dew, Melvyn John et al
Exxon Chemical Europe Inc.
P.O.Box 105
1830 Machelen (BE)

(56) References cited:
EP-A- 0 114 964
GB-A- 2 178 433

- DATABASE WPI Week 7944, Derwent Publications Ltd., London, GB; AN 79-79624B & JP,A,54 120 646 (DENKI KAGAKU KOGYO) 19 September 1979 cited in the application
- DATABASE WPI Week 8737, Derwent Publications Ltd., London, GB; AN 87-260136 & JP,A,62 179 543 (MITSUBISHI PETROCHEM.) 6 August 1987
- DATABASE WPI Week 8336, Derwent Publications Ltd., London, GB; AN 83-756419 & JP,A,58 129 034 (ASAHI CHEMICAL IND.) 1 August 1983
- DATABASE WPI Week 8041, Derwent Publications Ltd., London, GB; AN 80-72216C & JP,A,55 110 141 (MITSUBISHI PLASTICS) 26 August 1980
- PATENT ABSTRACTS OF JAPAN vol. 10, no. 148 (C-350)29 May 1986 & JP,A,61 009 448 (MITSUBISHI KASEI KOGYO) 17 January 1986

Printed by Jouve, 75001 PARIS (FR)

Description

This application is a Continuation-In-Part of U.S. Application Serial No. 08/013,518, filed Feb. 3, 1993.

FIELD OF INVENTION

This invention relates to thermoplastic elastomer blends of elastomeric block copolymers and certain olefin copolymers and, more specifically, to the fabricated films of the blends which exhibit high tensile strength and elasticity.

BACKGROUND OF THE INVENTION

Thermoplastic elastomers are readily commercially available and are fabricated as elastomeric films in products such as disposable diapers, leggins, waistbands and gloves. Typically, these elastomeric films have been made of elastomeric block copolymers, combinations of elastomeric block copolymers and liquid butadienes, combinations of elastomeric block copolymers and ethylene vinyl acetate copolymers, thermoplastic urethanes, ethylene-propylene rubbers (EP or EPR), including ethylene-propylene diene terpolymers (EPDM), natural rubbers and combinations of polyester copolymers and ethylene-vinyl acetate copolymers. Each of these materials has suitable properties for elastomeric films, such as low tensile set, low modulus, and high elongation, but each also has acknowledged deficiencies. For example, elastomeric films containing thermoplastic urethanes, copolyesters and/or ethylene vinyl acetate copolymers are expensive due to the cost of raw materials. The tensile set and modulus of films made of these well known elastomers are acceptable for many applications, but even greater advantages would be realized from films fabricated from elastomeric materials with lower tensile set and lower modulus.

It is well known to blend thermoplastic polymers in varying proportions with thermoplastic rubbers. Thermoplastic polymers such as polypropylene (meaning isotactic or crystalline polypropylene), polystyrene, polyethylene, ethylene-vinyl acetate copolymer, and polyurethane have been blended with thermoplastic rubber to effect compositions having varied thermoplastic and/or elastomeric properties.

The present invention relates to thermoplastic elastomer films made of elastomeric block copolymers and polyethylene/a-olefin copolymers. The relevant prior art to same includes the following:

A) U. S. Patent 4,476,180 describes elastomeric films comprising from about 40% to about 80% of a thermoplastic block copolymer of styrene-butadiene-styrene (S-B-S) and from about 20 to about 60% of an ethylene/vinyl acetate copolymer (EVA), the fabricated films of which demonstrate good tensile strength and elasticity. While these films demonstrate suitable properties for most elastomeric film applications, the shortcomings of these films are (1) a significantly reduced elasticity of the patented blend as compared to the elastic property of the pure elastic S-B-S copolymer; (2) difficulty in processing of the blend; and (3) typically excessive blocking of the S-B-S elastomeric copolymer. U. S. Patent 4,977,014 attempted reduction of these shortcomings by adding polystyrene to the '180 blend composition of the '180 patent.

B) Japanese patent application number 554-120646 published on September 19, 1979 discloses a composition of a styrene-butadiene elastomeric copolymer and ethylene/alphaolefin copolymer, the sole use of which composition was ineffective in film formation. This composition was rendered film-forming when a high styrenic styrene-butadiene copolymer was used as a third component. The ethylene/α-olefin copolymer has a density of 0.87 to 0.90, and is of low crystallinity.

While all of the cited elastomeric blend film art demonstrates certain advantages relating to processability, or physical characteristics such as softness, tensile strength or elasticity, they all fail to teach or appreciate the use of elastomeric block copolymer and linear low density polyethylene ("LLDPE") blends as demonstrated in the present invention. Consequently, the prior art elastomer/polyolefin blends retain certain deficiencies relating to film fabrication for apparel or healthcare use.

As any garments or healthcare products are worn, the elastic polymers used therein must have enough elastic strength to hold any of these items snugly in place. Conversely, an unworn garment or item must have a high degree of elastic recoverability so that the elastomeric polymer used therein returns essentially to an original shape during non-use. Additionally, any elastomeric films used in apparel items must also demonstrate a high degree of repeatability as any such items are worn over a long period of time. These conditions and constraints dictate the suitability of those elastomeric compositions of the prior art which can be fabricat d into articles for garment or wear use.

As indicated above, typical elastic materials utiliz d for clothing or healthcare applications include the thermoplastic elastomeric films of U.S. Patent 4,476,180 which are comprised of elastom ric block copolymers of monoalkenyl arenes (styrene) and conjugated dien s (butadi ne). These films generally xhibit good strength and lastic properties but

also undesirable xcessive blocking. Blocking is the tendency of a film to adhere to itself. When films made from block copolymers of monoalkenyl ar nes and conjugated dienes ar stored on a roll or in stacks, the film layers become difficult to unroll or unstack over a period to time due to their blocking tendency. Such blocking tendency can cause the film to tear when it is being unwound from a roll or being unstacked. To avoid such blocking it is generally necessary to add significant quantities of slip and anti-block agents to the film blend. The addition of these materials is undesirable because such material can accumulate on the film fabrication apparatus, particularly the rollers, and this accumulation can result in significant down time for machine cleaning.

It now has been found that the addition of certain linear low density ethylene/α-olefin copolymers to elastomeric block copolymers of monoalkenyl arenes and conjugated dienes results in films having substantially reduced blocking tendency while exhibiting optimum elastic properties.

BRIEF SUMMARY OF THE INVENTION

The instant invention is a thermoplastic elastomeric film comprising (a) from 20% to 70% of an a monoalkenyl arene-diene elastomeric block copolymer comprising from 8 to 55% by weight of monoalkyenyl arene and (b) from 30% to 80% of a linear low density ethylene/α-olefin plastomer having a density in the range from 0.86 to 0.90 g/cm^3, a molecular weight distribution in the range of 2 to 3.5, a melt index of between 0.2 - 1000 dg/min and an ethylene crystallinity of less than 35%.

The plastomer copolymers to be used in accordance with the present invention have very low ethylene crystallinity. The films made from blends of these low crystalline ethylene copolymers and elastomeric copolymers have the characteristics of high elasticity and low blocking tendency. These benefits occur because the instant film blends contain low crystalline plastomeric ethylene copolymers having certain characteristics of molecular weight distributions (M_w/M_n) (MWD), melt index (MI), density, and crystallinity.

The films of the present invention have improved elastic recovery over those films of the prior art and provide benefits and applications where both low modulus and excellent elastic recovery are necessary as in the case of elastic components of disposable diapers. The instant films exhibit a low blocking tendency and consecuently can be manufactured more efficiently and less expensively than other elastomeric films which require significantly more slip and anti-blocking additives for their processed blends.

The elastomeric films of this invention are films of 1,27 to 43,18 mm (5 to 15 mils) in thickness and may be produced by any well known film manufacturing processes such as these disclosed J.H. Briston and L.L. Katan in Plastic Films, published by John Wiley & Sons, New York (2nd ed. 1983). Commoniy known methods of producing film which may be utilized in the present invention include blowing, casting (extrusion and solvent), calendaring and extrusion methods, such as blow extrusion or slit die extrusion and cast embossed extrusion.

A preferred aspect of the present invention is directed to a film comprising from 20% to 70% of a monoalkenyl arene diene elastomeric block copolymer and from 30 to 80% of a linear low density polyethylene copolymer having a density in the range of from 0.88 to 0.90, a melt index of from .2 dg/min to 1000 dg/min, an MWD in the range of 2 to 3.5, and a CDBI greater than 45°C.

The invention further provides a method for producing an elastic film, said method comprising the steps:

(a) providing a blend of from 20 to 70% by weight of a monoalkenyl arene-diene elastomeric block copolymer, comprising 8 to 55% by weight of mono alkenyl arene and from 30 to 80% by weight of a linear low density ethylene/α-olefin copolymer, the co-polymer having a density in the range of 0.86 to 0.900 g/cm^3, a MWD in the range of 2 to 3.5, a melt index in the range of.2 dg/min to about 1000 dg/min, and an ethylene crystallinity less than 35%; and

(b) converting said plastomer/elastomeric block copolymer blend into a film by a film making process of slit-die extrusion, cast die extrusion, cast/embossed extrusion processing or by melt blowing said plastomer.

The invention further provides a method for producing the elastomeric film comprising extruding the blend composition through a die having a gap greater than 5 mils and less than 120 mils; (c) expanding the extruded film to a thickness of between 0.5 mils and 15 mils by application of differential pressure as exerted by a gas and (d) rapidly cooling the expanded extruded film.

The film produced by these methods may be oriented to a total draw down ratio of 12:1 to 100:1 through a blown film or cast film die.

BRIEF DESCRIPTION OF THE DRAWING

FIGURE 1 is schematic of the present invention showing the film of the present invention being made by a blown film apparatus and process, wherein the melted thermoplastic elastomer blend is blown into a tube and air cooled to

form th film.

DETAILED DESCRIPTION OF THE INVENTION

The thermoplastic elastomeric films of this invention comprise a blend of at least two copolymers. One copolymer is an elastomeric block copolymer containing blocks of a monoalkenyl arene copolymer and a conjugated diene polymer. The second component is selected from a group of highly amorphous thermoplastic ethylene copolymers having the primary characteristic of low crystallinity and low density. Optional ingredients which may also be included in the polymer blends of the present invention include small amounts of conventional anti-block concentrates and slip agents.

FIGURE 1 shows a schematic of a blown film extrusion apparatus 10 and process for preparing the present film. The thermoplastic elastic pellets are fed into hopper 11 of extruder 12 where the elastic pellets are heated to above their melting point. The heated and extruded material is then fed through a ring shaped die 13 where it is formed into a sleeve or tube shaped film (not shown). The tube or sleeve so formed is subsequently blown and air cooled by an air ring 14 to form a bubble 15 of blown film. The bubble 15 is cooled further and then collapsed by converging frame elements 16 and then rolled into a flattened tube 17 by nip rollers 18. The flattened film 17 is then rolled on through idle rollers 19 and 20 by take up roll 21 to form film roll 22. A slitter (not shown) is an optional station that slits film 17 into two sheets if desired.

The instant thermoplastic elastomer film blends are formulated such that they can be processed on conventional thermoplastic film making equipment such as that of Figure 1 or that used in a cast film processes. Thermoplastic elastomeric films produced with the instant blends are from about 1,27 mm (0.5 mils) to about 43,18 mm (15 mils) in thickness, preferably from about 2,54 to 7,62 mm (1 to 3 mils) in thickness.

ELASTICITY

"Unload power" is the technical measure of elastic strength and an important elastic tensile property for elastomeric films to be used in garment or other skinwear applications. For example, in diaper applications, the unload power of an elastomeric article provides indication of the retractive force which holds the elastomeric article such as a backsheet against the infant's body. In all elastomeric materials, the unload power is lower than the load power (the force required to extend the film strip). This difference shows up as a hysterisis (the differential of the force to extend and the force to hold in place) and is larger for synthetic elastomers than in the case of a natural rubber.

"Permanent set" also termed "tensile set" or "residual set" refers to the change between the length of al elastomeric material before and after its extension to a certain length for a certain time for a certain number of cycles. For example, it would be measured by the percent change in length of a film after extension of the film to 150%, 200% and 300% of its initial length through 2.5 cycles. Each cycle would consist of extending the film beyond its initial length, holding the film extending for a time period, releasing the extending force, and allowing the film to return for a time period.

THE ELASTOMERIC BLOCK COPOLYMER

The preferred elastomeric block copolymers contemplated for use herein are known materials having blocks of monoalkenyl arene polymer and blocks of conjugated diene polymer. The polymer blocks have the general configuration:

$$A - B - A$$

and are arranged such that there are at least two monoalkenyl arene polymer end blocks A and at a least one elastomeric conjugated diene mid block B. The monoalkenyl arene copolymer blocks comprise from 8% to about 55% by weight of the block copolymer. The molecular weight of the block copolymer is such that its melt index is less than about 100 as determined by ASTM Method D 1238 entitled "Standard Test Method for Flow Rates of Thermoplastics by Extrusion Plastomer" Condition E.

The term "monoalkenyl arene" includes those particular compounds of the benzene series such as styrene and its analogues and homologues including o-methyl styrene and p-methyl styrene, p-tert-butyl styrene, 1,3 dimethyl styrene p-methyl styrene in other ring alkylated styrenes, particularly ring methylated styrenes, and other monoalkenyl polycyclic aromatic compounds such as vinyl naphthalene, vinyl anthrycene and the like. For the present invention, the preferred monoalkenyl ar nes are monovinyl, monocyclic arenes such as styrene and p-methyl styrene, styr ne being particularly preferred.

It is critical to the present invention that th amount of monoalkenyl arene not exceed an amount of 55%, nor comprise an amount less than 8% by weight of the copolymer. Preferred amounts of monoalkenyl arene in th block

copolymer are from 25% to 35%. Optionally, the monoalkenyl arene will be in an amount of about 30%. If a monoalkenyl ar ne is used in xc ss of 55 weight percent, the block copolymer is too stiff for the instant blends. The elastomeric block copolymers are "oil extended" which is the addition of a hydrocarbon oil and allows for improved processability and softer films. The oils are added to the commercial elastomeric copolymers in amounts of between 10% to 40%.

The block B comprises homopolymers of conjugated diene monomers, copolymers of two or more conjugated dienes, and copolymers of one or more of the dienes with a monoalkenyl arene as long as the blocks B are predominantly conjugated diene units. The conjugated dienes preferably used herein contain from 4 to 8 carbon atoms. Examples of such suitably conjugated diene monomers include: 1,3 butadiene (butadiene); 2-methyl-1,3 butadiene; isoprene; 2,3 dimethyl-1,3 butadiene; 1,3 pentadiene (piperylene); 1,3 hexadiene and the like.

For the instant films, the preferred monoalkenyl arene polymer is polystyrene; and the preferred conjugated diene polymers are polybutadiene and polyisoprene, especially preferred being polybutadiene. The preferred elastomeric block copolymers are commercially available as linear tri-block copolymers (A-B-A) from the Shell Chemical Company, Polymers Division, Houston, Texas, under the tradename KRATON and from Dexco Polymers of Houston, Texas, under the family trademark VECTOR. Especially preferred are the linear tri-block copolymers having polystyrene end blocks and a polybutadiene mid-block (S-B-S). Most commercially preferred are oil extended polymers such as KRATON D2104 having a melt index of about 7 as determined by ASTM Method D 1238, Condition E and VECTOR 7400D, having a melt index of about 8.

The thermoplastic elastomeric films of the present invention may contain from about 20% to about 70% by weight of the elastomeric block copolymer; preferably from about 45% to about 65%; especially preferred being from about 50% to about 65%. The percentages herein are based on the total weight of the elastomeric film composition. As indicated, commercial grades of elastomeric block copolymers can be oil extended and the oil portion is not calculated as part of the percentage herein.

LINEAR LOW DENSITY PLASTOMER ALPHA-OLEFIN COPOLYMERS

As indicated above, the thermoplastic elastomeric film blends of the present invention are elastomeric block copolymers blended with amorphous linear low density ethylene/α-olefin copolymers. The ethylenela-olefin copolymers of the instant blends are hereinafter termed "PLASTOMERS". The term "PLASTOMER" as used herein refers generally to a class of ethylene based polymers with a density with less than about 0.90 g/cm^3 down to about 0.86 g/cm^3 at a weighted average molecular weight (Mw), Mw, of greater than 20,000.

The melt index of the plastomers utilized in the invention are such that the plastomers can be extruded into a desired end product. In the preferred embodiment, the MI must be such that the plastomer will have sufficient drawability as desired. Generally the melt index is in the range of about 0.2 dg/min to about 1000 dg/min, preferably, the MI is at least about 0.5 dg/min, more preferably at least about 1 dg/min, preferably the maximum MI is about 20 dg/min, more preferably about 5 dg/min. In another embodiment, the MI is in the range of about 0.5 dg/min to about 50 dg/min, and more preferably in the range of about 1 dg/min to about 5 dg/min. MI as measured herein was determined according to ASTM D-1238 (190/2.16). These linear low density ethylene/α-olefin copolymers have an ethylene crystallinity between 5 to 35% and preferably between 5 to 15%. Densities were measured using ASTM D-1505 procedure, except that they were additionally conditioned by holding the resin for 48 hours at ambient temperature (23°C) prior to density measurement.

The plastomer utilized in the elastomeric compositions of the present invention are selected from the group of polymers consisting of ethylene copolymerized with a C_3 to C_{20} α-olefins. The type of α-olefin comonomer selected for the plastomer herein will depend upon the type of film fabrication usage ultimately contemplated. Preferred α-olefins for use of comonomers in the plastomer polyethylene copolymers of the present film blends are C_3 to C_8 α-olefins, and the most preferred linear low density polyethylene copolymers are ethylene/propylene, ethylene/butene-1, ethylene/hexene-1, ethylene/hexene-1, ethylene octene-1, ethylene/4-methyl-l-pentene. Styrene may be included as a comonomer.

Typically, these plastomers will generally comprise in the range of about 65 mole percent to about 93 mole percent ethylene, based on the total moles of monomer. Preferably the amount of ethylene in these very low density copolymer plastomers ranges from about 68 to 91 mole percent. For complete effectiveness in the instant thermoplastic elastomeric film blends, the plastomers preferably have an ethylene crystallinity less than 35% and, optimally, less than 15%. Additionally, these plastomeric copolymers have a density in the range of 0.860 g/cm^3 to 0.90 g/cm^3 and preferably, an optimum density of 0.860 g/cm^3 to .875 g/cm^3.

The melt index (MI) of these plastomers is such that the plastomer can be extruded or blown into the desired film product. In addition, the MI must be such that the plastomer will have sufficient drawability as desired. Generally the melt index is in th range of about 0.2 dg/min to about 20 dg/min, preferably b tw en 1-10, and most desirably at about 2-6 dg/min.

The plastomers utilized in this invention have a molecular weight distribution such that the polymer will have the

desired drawability and be processable into the desired film end product. The ratio of M_w/M_n (polydispersity) is in the range of 2 to 3.5.

A key characteristic of the plastom rs us d in the elastomeric films of th present invention is their composition distribution. As is well known to those skilled in the art, the composition distribution of a copolymer relates to the uniformity of distribution of comonomer among the molecules of the copolymer. Metallocene catalysts are known to incorporate comonomer very evenly among the polymer molecules they produce. Thus, copolymers produced from a catalyst system having a single metallocene component have a very narrow composition distribution - most of the polymer molecules will have roughly the same comonomer content and within each molecule the comonomer will be randomly distributed. With certain exceptions, Ziegler-Natta catalysts generally yield copolymers having a considerably broader composition distribution and, consequently, comonomer inclusion will vary widely among the polymer molecules.

In order to achieve the molecular weight distribution ratios outlined above, it is essential that the plastomer used in the instant elastomeric blend composition be prepared from catalysts that will achieve the narrow molecular weight distribution required herein. As already indicated, metallocene catalysts are highly flexible in that, by manipulation of catalyst composition and reaction conditions, they can achieve and control the molecular weight distribution of the copolymers to achieve an extremely narrow molecular weight distribution or polydispersity (Mw/Mn) of about 2, to a broad distribution (as in a polydispersity of about 8). Exemplary of the development of these metallocene catalysts for the copolymerization of the ethylene and α-olefins of the instant plastomers are U. S. Patent 4,937,299 to Ewen et al.; 4,808,561 to Welborn et al.; 4,814,310 to Chang et al. All of these publications describe polymerization processes using single site metallocene catalysts (SSC).

Another family of catalysts which can achieve equivalent results are those Ziegler type catalysts containing vanadium halides and oxyhalides (e.g., VCl_4, $VOCl_3$, VBr_4); and such compounds wherein at least one of valences of the metal is saturated by a heteroatom (in particular oxygen or nitrogen) bound to an organic group, such as vanadium tribenzoylacetonate, vanadyl diacetylacetonates and the haloacetylacetonates, vanadyl trialcoholates and haloalcoholates, the tetrahydrofuranates, etherates, the aminates of vanadium tri- and tetrachloride and of vanadyl trichloride, and the pyridinates and quinolinates of vanadium tri- and tetrachloride and of vanadyl trichloride. Vanadium compounds which are insoluble in hydrocarbons may also be used in preparing the catalysts, particularly, the organic salts such as e.g., vanadium triacetate, tribenzoate, and tristerate.

Specific methods for making the instant ethylene/α-olefin copolymer plastomers are taught in U. S. Patent 4,871,705 to Hoel et al.. Utilizing single site metallocene catalysts of the cited prior art, the plastomer useful in the present elastomeric compositions can be produced in accordance with any suitable polymerization process, including a slurry polymerization, a gas phase polymerization, and a high pressure polymerization process.

CDBI is a measure of composition distribution. CDBI is defined as the weight percent of the copolymer molecules having a comonomer content. The CDBI of a copolymer is readily determined utilizing well known techniques for isolating individual fractions of a sample of the copolymer. One such technique is Temperature Rising Elation Fraction (TREF), as described in Wild, et al., J. Poly. Sci. Poly. Phys. Ed., vol. 20, p. 441 (1982), which is incorporated herein by reference.

To determine CDBI, a solubility distribution curve is first generated for the copolymer. This may be accomplished using data acquired from TREF techniques described above. This solubility distribution curve is a plot of the weight fraction of the copolymer that is solubilized as a function of temperature. This is converted to a weight fraction versus composition distribution curve. For the purpose of simplifying the correlation of composition with elution temperature the weight fractions less than 15,000 are ignored. These low weight fractions generally represent a trivial portion of the plastomer of the present invention. The remainder of this description and the appended claims maintain this convention of ignoring weight fractions below 15,000 in the CDBI measurements.

From the weight fraction versus composition distribution curve the CDBI is determined by establishing what weight percent of the sample has comonomer content within 25% each side of the median comonomer content. Further details of determining CDBI of a copolymer are known to those skilled in the art, see, for example, PCT Patent Application WO 93/03093, published February 18, 1993.

The composition distribution breadth index (CDBI) of the plastomers utilized in the present invention is generally 45 percent or higher, preferably, the CDBI is 50 percent or higher and more preferably, the CDBI is 60 percent or higher, and most preferably, 70 percent or higher.

The linear low density ethylene copolymers produced from the single site metallocene catalysts have been found to substantially reduce the blocking tendency of the instant elastomeric films containing them. Optimum blocking characteristics have been achieved with those elastomeric films comprising these plastomers and the styrene-butadiene-styrene copolymers sold as the VECTOR 7400 D s ries by Dexco Polymers. The advantage is the use of low slip concentrations, thereby reducing cost and improving final conversion effici ncy by reducing slip plat -out during lamination and by reducing the quantity of adhesive required to laminate the film to another substrate. Additionally, elastic recoverability and substantially reduced tensile s t were accomplish d with all metallocene engender d plastomers

and elastomeric copolymer blend films compositions of th present invention when compared to the compositions taught in the prior art.

As indicated above, the EVA/elastomeric copolymer blends of U. S. patent 4,476,180 represent state of the art th rmoplastic elastomeric film blend materials and are widely accepted as the most satisfactory film fabrication compositions presently available. It has now been found that permanent set of the instant plastomer/elastomeric copolymer compositions represents as much as a 60% improvement over the recovery compatibility of those ethyl vinyl acetate/ elastomeric copolymer compositions taught by U. S. Patent 4,476,180.

The linear low density ethylene/a-olefin copolymers referred to above have the characteristics of being low density and having low ethylene crystallinity giving them an amorphous crystalline structure and the physical characteristics of relatively high melt viscosity. This renders these copolymers generally miscible with the elastomeric block copolymers with which they are combined to form the film blends herein. While not to be construed as limiting, it is hypothesized that the ethylene/α-olefin copolymers disclosed herein possess so little ethylene crystallinity that there is very little deformation set when these molecules are stretched and hence the resulting hysterisis benefits when used in conjunction with elastomeric block copolymers to form the highly elastic films of the invention.

The amounts of plastomer in the present elastomeric films range from 30 to 80% and preferably between 25 to 50% by weight of the total composition of the film. These ranges of the plastomer component of the instant blends insure the necessary processability and elastomeric properties of these plastomer/ elastomeric block copolymer film blends.

OPTIONAL INGREDIENTS

Preferred thermoplastic elastomeric films of the present invention may contain from 0 to about 4% of commercial anti-block substances preferably from about 2% to about 3.5%. Preferred anti-block substances used in films of the present invention include the silicon based masterbatch sold as CM 19002 by Quantum Chemical Company.

Reduction in blocking in the films of the present invention can also be obtained by loading the film surface with small particles of powder such as talc, chalk, clay, silica, and similar materials. Powdered polymeric materials such as polytetrafluoroethylene can also be used to reduce blocking when applied to the surface of films of the present invention. Such film treatment can be used to reduce blocking alone or in combination with other anti-block methods described herein or otherwise known in the prior art. The quantity of powder anti-block substance commonly added to the surface of a film when used is from about 0.5 g/m^2 to about 5 g/m^2.

Anti-static agents may be incorporated in films of the present invention; examples of such agents included ethoxylated amines and quarternary amine salts having organic constituents of 12 to 18 carbon atoms in length. Agents of this type slowly diffuse to the surface of the film and, because of their ionic character, form an electrically conductive layer on the surface of the layer of the film. Anti-static agents commonly constitute from 1% to 5% of the weight of the films, when used.

While anti-blocking is a central characteristic of the present film blend, small amounts of slip agents will be incorporated into the films of the present invention to further reduce drag over rollers and other forming equipment. Examples of such agents are those commonly derived from amide fatty acids having from 12 to 22 carbon atoms. Such agents may augment the superior anti-blocking properties of the films of the present invention. Such slip agents are commonly incorporated in films from 0.05% to 3% of the weight of the films when used. Again, the present film blends are superior in anti-blocking characteristics thereby reducing the need for such slip agents, the reduction of block tendency rendering film production more efficient and less expensive.

In order to minimize degradation of films of the present invention during processing by extrusion or other techniques heat stabilizers and antioxidants may be added to the polymer formulations. Examples of heat stabilizers that may be used are organic phosphite compounds and other organic substances such as trihydroxy butyrophenone. When used, heat stabilizers and antioxidants are incorporated into the polymeric formulations at levels of 0.1% to 2.5% by weight.

Degradation of the films of the present invention by exposure to ultraviolet light can be moderated by the addition of photostabilizers. An example such photostabilizers are well known in the prior art and included derivatives of benzophenone. Such photostabilizers are generally incorporated in the polymer formulations at a level from 0.1% to 3% when used.

Pigments may also be added to the polymer formulations to impart a particular color to the resulting films. Pigments are typically added to the resin blend in the form of concentrates, formulated to improved dispersion of the pigment at levels of from 0.5% to 4% when used.

The optional constituents described here and above may be used alone or in combination with any or all of the other optional constituents in the present film bl nds.

Film Fabrication

The invention enables elastic materials of increased unload power and residual set to be prepared. According to ASTM definitions relating to rubbers, elastic materials are considered those materials which rapidly return to approximately their initial dimensions and shape after substantial deformation by a weak stress and release of the stress. The elastic materials of the invention are considered to be those which, when stretch to one and half to twice their original length (1.5-2X) at room temperature (18°C to 29°C), and held at 1.5-2X for one minute, will retract to less than 1.0X within one minute after the deforming force is released.

Elastic film having improved unload power and residual set can be produced by blown, cast or embossed extrusion processes. The film is formed by any suitable method well known in the art, or once formed, the film can be subjected to a combination of post orienting and/or annealing to effect changes in its unload power. Such methods of making film are discussed by the earlier cited J. H. Briston and L. L. Katan in Plastic Films, (2nd ed. 1983) and U.S. patent Numbers 4,436,520 and 5,066,526. Commonly know methods of producing film include casting (extrusion and solvent), is calendaring and extrusion methods, such as blow, slit extrusion or cast die extrusion, or cast embossed extrusion. A preferred preparation of the instant composition is the blown film process of Figure 1.

The invention is suitable for improving the unload power of thin elastic articles. Such thin elastic articles are commonly known as ribbon, tape, film, strip, sheet. The differences between these particular terms is generally dimensional. For example, tape is generally thought of as being narrower than film. For the purposes of this patent specification, the terms "ribbon", "tape", "film",, "sheet", and "strip" are generally interchangeable.

Regardless of the method of first producing the film, once made, the film can be used as is, or it can be further processed to improve unload power of the film. This further processing is accomplished by a combination of orienting and/or annealing the film. In one embodiment, the annealing is conducted at a temperature between the film softening point and melting point. Orientation of non-elastic films such as polypropylene, polystyrene, nylon and polyethylene terphthalate to improve clarity, impact strength and particularly in the case of polypropylene, its barrier properties, is well known in the art. The orienting and annealing of the film may be carried out monoaxially in the machine direction (MD) or the traverse direction (TD) or in both directions (biaxially) either simultaneously or sequentially using conventional equipment and processes following cooling of the film.

Blown films are preferably stretched in machine direction or in both directions. Cast films are preferably stretched in the machine direction. Generally, for orientation in the machine direction, the film is passed around two rollers driven at different surface speeds and finally to take up roller. The second driven roller which is closest to the take up roll is driven faster than the first driven roller. As a consequence, the film is stretched between the driven rollers. Conventional "godet" stands as are well known in the art may also be utilized.

Film orientation may also be carried out in a tentering device with or without machine direction orientation to impart transverse direction orientation in the film. The film is gripped by the edges for processing through the tentering device. For most final applications, the film is monoaxially oriented in the machine direction.

The morphology of the instant elastomer/plastomer films can be viewed as a matrix of amorphous material interspersed with crystallites. For orienting, it is generally necessary that the film be heated to between its softening point and its melting point. This heating is necessary to allow extension or orientation to be induced into the film. Since the temperature is between the film softening point and melting point, the smaller imperfect crystallites will melt, whereas larger more perfect crystallites of the plastomer will remain. The molecules in the amorphous matrix become oriented or extended depending on the draw ratio and other material and fabrication parameters.

The film of the invention may be annealed at a temperature between the film softening point and melting point. The annealing step is necessary to anneal or perfect the crystallites that survived the orienting step and to relax out stresses. This annealing aids in maintaining the orientation or extension induced in the orienting step. The annealing temperature is preferably less than the orienting temperature. Generally once the film leaves the annealing step, ambient cooling is sufficient. In most cases, the film from the annealing step is then spooled in a winding unit.

Industrial Applicability

The thermoplastic elastomeric films of the present invention may be used in a wide variety of applications where thin, elastic material would be useful. Such films are particularly useful as low cost elastic members for disposable wearing apparel such as diapers, training pants, feminine hygiene devices, medical gowns, gathered laminate garments, non-woven head bands, sports apparel, bandages and protective clothing.

EXAMPLES

The following examples illustrate preferred embodiments of the inv ntion in comparison to similar standard compositions not employing the plastomeric olefin copolym rs illustrated in the thermoplastic lastomeric film blends of

the present invention. All experiments were conducted with the materials indicated in the tables. All examples employed a styrene-butadiene elastomeric block copolymer in th commercial form of Shell's KRATON D 2104 and Dexco's VECTOR 7400D which was blended with the olefin copolymers according to the pr sent invention.

A. COMPOSITION

The character and commercial source of the elastomeric and plastomeric copolymer resins used in the examples are listed in the following table.

TABLE 1

RESIN	RESIN TYPE	MI (DG/MIN)	DENSITY (G/CM^3)	COMONOMER	SUPPLIER
KRATON D-2104	SBC	4.25	.930	SBS	SHELL
VECTOR 7400D	SBC	8.0	.930	SBS	DEXCO
LD-767	EVA	3.2	-	28% VA	EXXON
XS-12.04	EMA	3.0	-	28% MA	EXXON
TAFMER P0480	MITSUI	1.0	.867	EP	MITSUI
TAFMER P0280	MITSUI	3.0	.867	EP	MITSUI
TAFMER P0480	MITSUI	8.0	.867	EP	MITSUI
EXACT WS-9905	EXXPOL	4.1	.874	EB	EXXON
EXACT 4049	EXXPOL	4.5	.873	EB	EXXON
MBX-6	MB	8.6	1.176	SLIP = 3% A/B = 35% A/O = 0.2% CARRIER = LDPE	EXXON

The compositions employed in the following examples contain an additive package of 0.2% of IRGANOX 1076 stabilizer sold by Ciba-Geigy Corporation, 0.3% of Eucaramide Slip Crodamide ER sold by Humko Chemical and 3.5% of Superfloss Silica anti-blocking agent sold by Manville Corporation. The anti-block was introduced in the form of a 50/50 (LDPE/anti-block) masterbatch (CM 19002) supplied by Quantum Chemical Company, for hot melt blend formulations. The melt index of the film compositions or components was determined according to ASTM Method D 1238, condition E as indicated.

B. COMPOUNDING

All formulations identified in Table III, Examples 6-11, were hot melt compounded on a 57 mm twin screw ZSK Extruder manufactured by Werner Pfleiderer at melt temperatures not exceeding 176 °C (350°F) The extruder has a length diameter ratio (L/D) of 24:1. Feed rates ranged from 500 to 300 lbs/hr and water temperatures ranged from 25.5 (78) to 12.7°C (55°F) The blends of Table II were dry blended as indicated.

C. FILM FABRICATION

Film was produced on a 3,81 cm (1 1/2 inch) Egan Blown Film extruder having 24:1 L/D and a 7,62 cm (3 inch) die. The melt temperature of the film blend was about 160°C (320°F). The BUR was 2:1 and films of about $5*10^{-3}$ cm (2 mil) thickness resulted.

The blowup ratio of blown films is calculated as the ratio of the total lay-flat with blown film to the circumference of the inner circle of the film dye.

The blown film conditions in the Egan Line extrusion process for the two sets of samples subjected to the respective 200% and 150% extensions are outlined in Tables II and III as follows.

Two examples of films fabricated for data of Table VI were prepared on a 11,4 cm (4 1/2 inch) commercial film line at Exxon Chemical Company in Lake Zurich, Illinois.

94RWM030.DOC/GZE

TABLE II

BLOWN FILM EXTRUSION CONDITIONS FOR SAMPLES SUBJECTED TO 200% EXTENSION

SAMPLE ID	BUR	DIE GAP (MIL)	YAG (MIL)	EXT SPEED (RPM)	EXT. LOAD (AMPS)	EXT. PRESS (PSI)	FLH (IN)	MELT TEMP °C (°F)	SCREEN PACK
001 (CONTROL) KRATON D2104, SBC 28% EVA	2.1	35	2.05	30	20	1450	9.5	160 (320)	40/120/40
002 KRATON D2104, SBC 28% EMA	2.1	35	2.37	30	22	1150	9.5	181 (358)	40/120/40
003 KRATON D2104, SBC 28% TAFMER P0480	2.1	35	2.40	30	28	2100	10	210 (410)	40/120/40
004 KRATON D2104, SBC 28% TAFMER P0280	2.1	35	2.32	30	25.5	1600	10	210 (410)	40/120/40
005 KRATON D2104, SBC 28% TAFMER P0180	2.1	35	2.19	30	26	1650	9.5	192 (378)	40/120/40

NOTE: ALL BLEND FORMULATIONS ARE DRY BLENDED WITH A SLIP, ANTIBLOCK MASTERBATCH (MBX-6). FILM FABRICATED ON A 1 1/2", 24:1 L/D FILM EXTRUDER.

1MIL = 2.54×10^{-3} cm
1 PSI = 6894 N/m^2
1IN = 2.54 cm

94RWM030.DOC/GZE

TABLE III

BLOWN FILM EXTRUSION CONDITIONS FOR SAMPLES SUBJECTED TO 150% EXTENSION

SAMPLE ID	BUR	DIE GAP (MIL)	YAG (MIL)	EXT SPEED (RPM)	EXT. LOAD (AMPS)	EXT. PRESS (PSI)	FLH (IN)	MELT TEMP °C (°F)	SCREEN PACK
006 (CONTROL) KRATON D2104, SBC 28% EVA	2.1	35	2.19	30	23	1770	9	160 (320)	20/40/80/20
007 (CONTROL) KRATON D2104, SBC 28% EVA	2.1	50	2.89	30	22	1090	9.5	163 (325)	20/40/20
008 KRATON D2104, SBC 28% EXXPOL	2.1	35	2.31	30	29	2460	10	160 (320)	20/40/80/20
009 KRATON D2104, SBC 46% EXXPOL	2.1	35	2.25	30	32	2660	10	160 (320)	20/40/80/20
0010 VECTOR 7400D, SBC 28% EXXPOL	2.2	50	2.68	30	29	1630	12.5	164 (327)	20/40/20
0011 VECTOR 7400D, SBC 46% EXXPOL	2.2	50	2.63	30	29	1580	12.5	164 (327)	20/40/20

NOTE: ALL BLEND FORMULATIONS HOT MELT COMPOUNDED ON A TWIN SCREW EXTRUDER WITH SLIP, ANTIBLOCK MASTERBATCH. FILM FABRICATED ON A 1 1/2", 24:1 L/D FILM EXTRUDER.

1MIL= 2.54×10^{-3} cm

1 PSI = 6894 N/m^2

1IN - 2.54 cm

D. **HYSTERESIS**

The ultimate tensile strength and elongation were determined according to ASTM D-882-81 Method using an INSTRON Model 1122 Tester. The tensile properties of the film were measured in the direction of extrusion of the film (machine direction, MD); and in the direction perpendicular to the direction of the extrusion (crossmachine direction, CD or - traverse direction {TD}). Test specimens were cut along the direction of extrusion of the film (MD) and along th traverse direction in segments of 25 mm (1 inch) wide and 150 mm (6 inches) long.

The hysteresis testing is an Exxon variation of a procedure described by DuPont in its brochure on its is polyether urethane elastic product, T-722A. In the Exxon variation, 25 mm x 150 mm (1 inch x 6 inch) strips are subjected to a strain rate of 150% or 200% or 300% with a jaw gap separation of 50 mm (2") and crosshead speed of 500 mm/min (20"/min.) the hysteresis stress/strain curve is plotted on a chart also travelling a 500 mm/min (20"/min.). Both the extension and retraction crosshead speeds (500 mm/min.) (20"/min.) were the same and performed on an Instron model 1123. The film was held for 60 seconds at maximum extension and then retracted and held for 30 seconds relaxation prior to the next cycle. This was repeated 2 1/2 times. Key pieces of information that are extracted from these stress/strain plots are the maximum force (modulus) of each cycle, the residual set or permanent set (the degree of deformation as measured by the point of stress divided by total strain/cycle) , and the unload force or contractive power as measured from the last retraction cycle at various elongations. Generally, five specimens were tested for each sample, with mean values over these samples developed.

For the films of the present invention, the preferred hysteresis properties which are obtained are as follows:

Permanent set (%) (obtained through use of a modification of ASTM D-1682 wherein the stretching is cycled rather than continued through film failure) (150% extension, one cycle, MD): preferably less than 40%, more preferably in the range of 5 to 25%, most preferably less than 20%, and/or

Permanent set (%) (150% extension, 1 cycle, TD): preferably less than 40%, more preferably in the range of 5 to 25%, most preferably less than 20% and/or;

Permanent set (%) (200% extension, 1 cycle, MD): preferably less than 45%, more preferably less than 25%, most preferably 5-15%; and/or

Permanent set (%) (200% extension, one cycle, TD): preferably less than 45%, more preferably less than 25%, most preferably in the range of about 5-15%; and/or

Permanent set (%) (300% extension, 1 cycle, MD): preferably less than 50%, more preferably less than 40%, most preferably 15-30%; and/or

Permanent set (%) (300% extension, one cycle, TD): preferably less than 50%, more preferably less than 40%, most preferably in the range of about 15-30%; and/or

Table 4 lists comparative data for the following. Examples 1-5 with Example 1 being the control using the standard blend formulations. These examples were dry blended, then extruded on a 3.81 cm (1 1/2") Egan blown film lab line. Melt strength, film appearance, and openability, were measured on line. Hysterisis testing was preferred at 200% extension in order to compare improvements to elastic recoverability.

EXAMPLE 1

Blend Formulation:	
Component	**Percentage**
KRATON D 2104	63%
LD 767.36	27%
MBX - 6	10%

The material extruded satisfactorily with good melt strength as indicated by the observed bubble stability. The collapsed film was peeled with no sticking or fusing, thereby qualitatively determining "openability" as good and given an "A" rating (based on an A, B, C, D scale with "A" being good and "D" being poor). The film appearance rating (FAR)

was slightly grainy and qualitativ ly given a "B" rating based a scale which qualifies a totally clear film as an "A" rating while an opaque film would be rendered a "D". This film is the "control" and will be used as the comparison hereinafter.

EXAMPLE 2

Blend Component	Percentage
KRATON D 2104	63%
XS 12.04	27%
Ethyl Methyl Acrylate ("EMA") MBX - 6	10%

The film produced had a less grainy appearance and rated a FAR of "B". Openability was slightly less than Example 1 and rated a "B" to "C". Elastic recoverability was slightly improved over the control. The MD tensile set was 20% vs 22.6% (13% improvement) while the TD had a 17% improvement (18% vs. 21.2%).

EXAMPLE 3

Component	Percentage
KRATON D 2104	63%
TAFMER P0480	27%
MBX - 6	10

The material processed well with observed excellent bubble stability and received a FAR rating of "A". The openability was slightly less ("B") than the control but tensile set was substantially improved. The MD set was 14.1% vs. 22.6% (60% improvement) while the TD set displayed a 35% improvement (15.7% vs. 21.2%).

EXAMPLE 4

Component	Percentage
KRATON D 2104	63%
TAFMER P0280	27%
MBX - 6	10%

Good extrusion performance with an excellent FAR rating of "A" and comparable openability to the control thereby deserving of an "A" rating. Again the tensile set properties were substantially improved over the control. The MD permanent set had an improvement of 50% (15.1% vs. 22.6%) while the TD had an improvement of 39% (15.3% vs. 21.2%).

EXAMPLE 5

Component	Percentage
KRATON D 2104	63%
TAFMER P0180	27%
MBX - 6	10%

The material was very splitting and broke upon extension in the TD. The FAR rated a "C" and openability rated a "B". The tensile set could not be measured in the TD but the MD had a 53% improvement over the control (14.8% vs. 22.6%).

The results of the first five examples are outlined in Table IV. Example 2 utilized EMA as a polyolefin component of the elastomeric blend to illustrate the us of another known component commonly cited, but not commercially preferable, for use in elastomeric blends. The overall conclusions reached for those specific embodiments of the invention in Examples 3-5 are that substantial improvements to tensile s t (lastic r coverability) can be achi ved by replacing

the EVA component of the standard commercial blend as taught in prior art U. S. Pat nt 4,476,180, with a LLDPE plastomer copolymer such as the TAFMER P0480 and P0280 copolymers of Mitsui Corporation of Japan. As much as a 60% improvement has been demonstrated for t nsile set (recoverability) over the control while maintaining comparable modulus and extrusion process performance in the preparation of the films as illustrated in the data of Table IV. Note that the recoverability of the film of Example 2 utilizing EMA demonstrated a tensile set which improved slightly over the EVA control, but was not as impressive as Examples 3-5 utilizing the LLDPE's of the present invention.

WIN/94RWM030.DOC/GZE

TABLE IV

HYSTERESIS RESULTS @ 200% EXTENSION

SAMPLE ID		BUR	DIE GAP (MIL)	YAG (MIL)	MODULUS (1) (G)	MODULUS (2) (G)	% TENSILE SET (1) (%)	% TENSILE SET (2) (%)	UNLOAD FORCE (G) 25%	UNLOAD FORCE (G) 50%	UNLOAD FORCE (G) 200%
001 (CONTROL) KRATON D2104, SBC 28% EVA	MD	2.1	35	2.05	313	270	18.7	22.6	--	21.2	227
	TD				216	193	17.4	21.2	--	17.9	164
002 (CONTROL) KRATON D2104, SBC 28% EMA	MD	2.1	35	2.37	361	311	17.7	20.0	--	29.7	262
	TD				215	196	15.3	18.1	--	17.7	162
003 KRATON D2104, SBC 28% TAFMER P0480	MD	2.1	35	2.40	308	257	12.1	14.1	12.1	49.3	228
	TD				215	193	13.8	15.7	--	33.3	169
004 KRATON D2104, SBC 28% TAFMER P0280	MD	2.1	35	2.32	256	214	13.1	15.1	5.1	36.7	189
	TD				166	145	12.5	15.3	2.3	26.8	122
005 KRATON D2104, SBC 28% TAFMER P0480	MD	2.1	35	2.19	203	164	12.5	14.8	6.7	28.7	147
	TD				Broke	Broke	Broke	Broke	Broke	Broke	Broke

1MIL= 2.54×10^{-3} cm

The following Table V lists comparative hysteresis data for Examples 6 through 11 at 150% extension. All samples wer hot melt compounded on a 57 mm Zsk twin scr w extruder described previously. Compounds were then run on a 3,81 cm (1 1/2") Egan blown film line using both a $88,9 \cdot 10^{-3}$ cm (35) and 0,127 cm (50 mil) die gap. Film appearance, openability and bubble stability were measured qualitatively on line. Hysteresis testing was performed at 150% extension per the previously described method herein in order to compare improvements to elastic recoverability and any improvements to the process.

Comparisons were made with comparable die gaps. Therefore, Example 8 demonstrates a 22% improvement to tensile set over the control in Example 6 using the same amount of LLDPE (28%). Example 9 demonstrates comparable modulus and tensile set to the control of Example 6 using elevated amounts of LLDPE (48%). Similar results are obtained when comparing Example 7 with Examples 10 and 11.

WIN/94RWM030.DOC/GZE

TABLE V

HYSTERESIS RESULTS @ 150% EXTENSION

SAMPLE ID		BUR	DIE GAP (MIL)	YAG (MIL)	MODULUS (1) (G)	MODULUS (2) (G)	% TENSILE SET (1) (%)	% TENSILE SET (2) (%)	UNLOAD FORCE (g) 25%	UNLOAD FORCE (g) 50%	MI (DG/MIN)	DENSI. (g/cm³)
006 (CONTROL) KRATON D2104, SBC 28% EVA	MD	2.1	35	2.19	304	262	---	11.1	---	---	4.4	.949
	TD				286	265	---	10.3	---	---		
007 (CONTROL) KRATON D2104, SBC 28% EVA	MD	2.1	50	2.89	554	479	11.2	13.2	37	109	4.1	.941
	TD				289	265	12.5	14.4	21	67		
008 KRATON D2104, SBC 28% EXXPOL	MD	2.1	35	2.31	292	267	---	9.13	---	---	---	---
	TD				362	330	---	8.57	---	---		
009 KRATON D2104, SBC 48% EXXPOL	MD	2.1	35	2.25	309	278	---	12.9	---	---	3.1	.926
	TD				342	317	---	12.6	---	---		
0010 VECTOR 7400D, SBC 28% EXXPOL	MD	2.2	50	2.68	480	412	8.5	10.5	74	145	2.8	.920
	TD				244	224	11.1	13.1	39	82		
0011 VECTOR 7400D, SBC 48% EXXPOL	MD	2.2	50	2.63	451	398	11.1	13.1	36	109	2.7	.916
	TD				368	330	12.5	14.4	18	85		

1MIL= $2{,}54 \times 10^{-3}$ cm

EXAMPLES 6 & 7 (Controls)

Component	Percentage
KRATON D 2104	63.7%
LD 767.36	28.8%
Spectrathene (CM 19002)	7.0%
Euracamide	.3%
IR 1076	.2%

The Example 6 fabrication of the controls for the 150% hysteresis testing in Table V was performed using a $88,9*10^{-3}$cm (35 mil) die gap while Example 7 used a 0,127 cm (50 mil) gap. Both had good bubble stability and FAR "A". The film appearance was improved over dry blends of Example 1 in that they displayed no grainy appearance. Openability was good but did display some blocking ("B" rating). Permanent set was somewhat better using the $88,9*10^{-3}$cm (35 mil) die gap for Example 6 vs. 0,127 cm (50 mil) gap for Example 7. Also the MD modulus was higher for Example 7 vs. 6, but TD modulus was comparable.

EXAMPLE 8

Component	Percentage
KRATON D 2104	63.7%
EXXPOL WS-9905	28.8%
Spectrathene (CM 19002)	7.0%
Euracamide	.3%
IR 1076	.2%

Film appearance (FAR "A") and bubble stability were excellent. Film openability was substantially superior to the control and given an "A+" but the motor load and pressure were higher. MD tensile set was 22% improved (9.13% vs. 11.1%) over the control Example 6 (Control). An unexpected finding was the improvement to openability using the EXXPOL polymer as a replacement to the commercially accepted EVA. This use of the EXXPOL LLDPE in place of the standard EVA will not only improve the processability, but will allow reduced slip levels, thus saving additive costs and downtime for downstream converters due to slip build up.

EXAMPLE 9

Component	Percentage
KRATON D 2104	46.25%
EXXPOL WS-9905	46.25%
Spectrathene (CM 19002)	7.0%
Euracamide	.3%
IR 1076	.2%

Again bubble stability and FAR were excellent ("A" FAR rating) and openability was significantly improved over the controls and earned an "A++". Tensile set and modulus were comparable to the control of Example 6 at $88,9*10^{-3}$cm (35 mil) die gap. The advantage over the Example 6 control is the reduced amount of slip agent and SBC component, thus reducing cost of fabricating the film.

EXAMPLE 10

Component	Percentage
VECTOR 7400D	63.7%
EXXPOL W5-9905	28.8%
Spectrathene (CM 19002)	7.0%
Euracamide	.3%
IR 1076	.2%

This compound was compared against the Example 7 Control using the 0,127 cm (50 mil) die gap. Bubble stability and FAR were excellent ("A"). Film openability was significantly better than all other blends when the EXXPOL SSC and VECTOR SBC from the Dexco Company were compounded together and rated an A+++. Also the modulus and tensile set of this particular blend were substantially improved over the control (16% and 26% respectively) while the unload force (contractive power) was comparable to the commercially satisfactory controls. The unexpected finding was the improved openability for the VECTOR SBC EXXPOL's blend compared with the controls employing the same additive package.

EXAMPLE 11

Component	Percentage
VECTOR 7400D	46.25%
EXXPOL WS-9905	46.25%
Spectrathene (CM 19002)	7.0%
Euracamide	.3%
IR 1076	.2%

Film processability was comparable to the control (Example 7) but had somewhat higher load and pressure. The openability was comparable to Example 10 and substantially better than the EVA/KRATON blends. Modulus and tensile set were also comparable to the control showing that comparable properties can be achieved versus the control but at reduced SBC and slip additive levels which will substantially reduce costs and save downtime for convertors using embodiments of this invention.

EXAMPLE 12

COMPONENT	PERCENTAGE
VECTOR 7400D	60%
LD 767.36	32.1%
CM 19002	7%
EURACAMIDE	.7%
IR 1076	.2%

EXAMPLE 13

COMPONENT	PERCENTAGE
VECTOR 7400 D	60%
EXACT 4049	32.6%
CM 19002	7%
EURACAMIDE	.2%
IR 1070	.2%

In both Examples 12 and 13, samples were produced on a commercial blown film line. The samples were tested at 300% xtension in the travers direction.

In Table VI, the results of the comparative hysteresis data are listed. As shown, the tensile set of Example 13 (Exxpol Plastomer) was 22% compared to the 38% for th sample of 12 (EVA) demonstrating a 72% improvement in the tensile set of the SBS/Exxpol plastomer film.

WIN/94RWM030.DOC/GZE

TABLE VI

Hysteresis Results @ 300% Extension (TD)

SAMPLE ID	YAG MIL	MODULUS GRAMS	%TENSILE SET (%)
012 Vector 7400D EVA	2.664	545	38
013 Vector 7400D Exact 4049	2.651	323	22

1 mil = $2{,}54 \times 10^{-3}$ cm

The overall conclusions reached for th se specific embodiments of the invention ar that improvements to openability can be achieved by replacing the EVA with SSC EXXPOL plastomers. Also, substantial improvements to tensile set (elastic recoverability) can be achieved by replacing the KRATON SBC from Shell with the VECTOR 7400D SBC from Dexco. Ideally, the overall improvements afforded with the EXXPOL and Dexco VECTOR SBC used in combination not only improve tensile set, but processability as well. The improved openability afforded by these blends will not only reduce costs because of unnecessary additives (slip agents) but reduction in the amount of the SBC component as well. This particular embodiment will prove beneficial to convertors who use film produced from this invention in that reduced slip levels will equate to longer run time due to reduced slowdowns caused by slip buildup.

Claims

1. A thermoplastic elastomeric film comprising:

   a. from 20 to 70% by weight of a monoalkenyl arene-diene elastomeric block copolymer comprising 8 to 55% by weight of monoalkenyl arene

   and b. from 30 to 80% of a linear low density ethylene/α-olefin copolymer, the copolymer having a density in the range of 0.86 to 0.900 g/cm^3 (as determined using ASTM 1505 according to the description), a MWD in the range of 2 to 3.5, a melt index in the range of .2 dg/min to 1000 dg/min (measured according to ASTM D-1238 190/2.16 and an ethylene crystallinity less than 35%.

2. The film of claim 1 where in the comonomer of the ethylene copolymer comprises ethylenically unsaturated olefin (s) having from 3 to 20 carbon atoms.

3. The film of claim 2 wherein the comonomer comprises one or more of propylene, butene-1, hexene-1, octene-1, 4-methyl-1-pentene, and styrene.

4. The film of any of the preceding claims where in the copolymer has a density in the range of 0.86 to 0.90 g/cm^3.

5. The film of any of the preceding claims wherein the polyethylene copolymer has a CDBI greater than 45% (measured by TREF as described in the description).

6. The film of any of the preceding claims where in the elastomeric block copolymer is a styrene-butadiene copolymer.

7. The film of any of the preceding claims where in the elastomeric block copolymer is present in amounts of between 45% and 65% by weight.

8. The film of any of the preceding claims where in the ethylene copolymer is present in amounts of between 20% to 60% by weight.

9. The film of any of the preceding claims where in the elastomeric copolymer is present in amounts of between 45 to 65% by weight and the ethylene copolymer is present in amounts of between 25 and 50% by weight.

10. The film of any of the preceding claims wherein the elastomeric block copolymer is a styrene-isoprene copolymer.

11. The film of any of the preceding claims in which the permanent set, (as determined by ASTM D-1682 as described in the description) after one cycle of 150% extension in the machine or traverse direction, is below 40%.

12. The film of any of the preceding claims in which the permanent set, after one cycle of 150% extension in the machine or traverse direction, is between 5-25%.

13. The film of any the preceding claims in which the permanent set, after one cycle of 300% extension in the machine or traverse direction, of less than 50%.

14. The film of claim 13 in which th tensil set is less than 40%.

15. The film of any of the preceding claims in which the permanent set, after one cycle of 200% extension in the

machine or traverse direction, is betw en 5-15%.

16. The film of any of the preceding claims having:

(a) a permanent set, after one cycle of 150% extension in the machine or traverse direction of less than 20%.

(b) a permanent set, after one cycle of 200% extension in the transverse direction of less than 25%; and

(c) a permanent set, after one cycle of 300% extension in the transverse. direction of less than 40%.

17. A method for producing an elastic film, said method comprising the steps:

(a) providing a blend from 20 to 70% by weight of a monoalkenyl arene-diene elastomeric block copolymer, comprising 8 to 55% by weight of monoalkene arene, and from 30 to 80% by weight of a linear low density ethylene/α-olefin copolymer, the co-polymer having a density in the range of 0.86 to 0.900 g/cm^3. a MWD in the range of 2 to 3.5, a melt index in the range of.2 dg/min to 1000 dg/min, and an ethylene crystallinity less than 35%; and

(b) converting said plastomer/elastomeric block copolymer blend into a film by a film making process of slit-die extrusion, cast die extrusion, cast/embossed extrusion processing or by melt blowing said plastomer.

18. The method of claim 17 wherein the film conversion is a die castings process comprising:

(a) extruding the blend composition through a die having a gap greater than $12{,}7 \cdot 10^{-3}$ cm (5 mils) and less than 0,304 cm (120 mils) and

(c) rapidly cooling the expanded film.

19. The method of claim 17 or claim 18 wherein the said film is oriented to a total draw down ratio in the range of 2:1 to 100:1 through a blown film or cast film die.

Patentansprüche

1. Thermoplastische elastomere Folie, die

a. 20 bis 70 Gew.% elastomeres Monoalkenylaren/Dien-Blockcopolymer, das 8 bis 55 Gew.% Monoalkenylaren umfaßt, und
b. 30 bis 80 % lineares Ethylen/α-Olefin-Copolymer mit niedriger Dichte im Bereich von 0,86 bis 0,900 g/cm^3 (bestimmt unter Verwendung von ASTM 1505 gemäß der Beschreibung), einer MWD im Bereich von 2 bis 3,5, einem Schmelzindex im Bereich von 0,2 dg/Min bis 1000 dg/Min (gemessen gemäß ASTM D-1238 (190/2,16) und einer Ethylenkristallinität von weniger als 35 % umfaßt.

2. Folie nach Anspruch 1, bei der das Comonomer des Ethylencopolymers ethylenisch ungesättigtes Olefin oder ethylenisch ungesättigte Olefine mit 3 bis 20 Kohlenstoffatomen umfaßt.

3. Folie nach Anspruch 2, bei der das Comonomer ein oder mehrere aus Propylen, Buten-1, Hexen-1, Octen-1, 4-Methyl-1-penten und Styrol umfaßt.

4. Folie nach einem der vorhergehen den Ansprüche, bei der das Copolymer eine Dichte im Bereich von 0,86 bis 0,90 g/cm^3 hat.

5. Folie nach einem der vorhergehenden Ansprüche, bei dem das Polyethylencopolymer einen CDBI von größer als 45 % aufweist (gemessen mittels TREF, wie in der Beschreibung beschrieben).

6. Folie nach inem der vorhergehenden Ansprüche, bei der das lastomere Blockcopolymer Styrol/Butadien-Copolymer ist.

7. Folie nach inem der vorhergehenden Ansprüche, bei der das elastomer Blockcopolymer in Mengen zwischen 45 und 65 Gew.% vorhanden ist.

8. Folie nach einem der vorhergehenden Ansprüche, bei der das Ethylencopolymer in Mengen zwischen 20 und 60 Gew.% vorhanden ist.

9. Folie nach einem der vorhergehenden Ansprüche, bei der das elastomere Copolymer in Mengen zwischen 45 und 65 Gew.% vorhanden ist und das Ethylencopolymer in Mengen zwischen 25 und 50 Gew.% vorhanden ist.

10. Folie nach einem der vorhergehenden Ansprüche, bei der das elastomere Blockcopolymer Styrol/Isopren-Copolymer ist.

11. Folie nach einem der vorhergehenden Ansprüche, bei der die bleibende Verformung (bestimmt gemäß ASTM D-1682, wie in der Beschreibung beschrieben) nach einem Zyklus von 150 % Dehnung in Maschinen- oder Querrichtung unter 40 % beträgt.

12. Folie nach einem der vorhergehenden Ansprüche, bei der die bleibende Verformung nach einem Zyklus von 150 % Dehnung in Maschinen- oder Querrichtung zwischen 5 und 25 % beträgt.

13. Folie nach einem der vorhergehenden Ansprüche, bei der die bleibende Verformung nach einem Zyklus von 300 % Dehnung in Maschinen- oder Querrichtung weniger als 50 % beträgt.

14. Folie nach Anspruch 13, in der die Zugverformung weniger als 40 % beträgt.

15. Folie nach einem der vorhergehenden Ansprüche, bei der die bleibende Verformung nach einem Zyklus von 200 % Dehnung in Maschinen- oder Querrichtung zwischen 5 und 15 % liegt.

16. Folie nach einem der vorhergehenden Ansprüche mit

(a) einer bleibenden Verformung nach einem Zyklus von 150 % Dehnung in Maschinen- oder Querrichtung von weniger als 20 %;
(b) einer bleibenden Verformung nach einem Zyklus von 200 % Dehnung in Querrichtung von weniger als 25 % und
(c) einer bleibenden Verformung nach einem Zyklus von 300 % Dehnung in Querrichtung von weniger als 40 %.

17. Verfahren zur Herstellung von elastischer Folie, bei dem in Stufen

(a) ein Gemisch aus 20 bis 70 Gew.% elastomerem Monoalkenylaren/Dien-Blockcopolymer bereitgestellt wird, das 8 bis 55 Gew.% Monoalkenaren und 30 bis 80 Gew.% lineares Ethylen/α-Olefin-Copolymer mit niedriger Dichte umfaßt, wobei das Copolymer eine Dichte im Bereich von 0,86 bis 0,900 g/cm^3, eine MWD im Bereich von 2 bis 3,5, einen Schmelzindex im Bereich von 0,2 dg/Min bis 1000 dg/Min und eine Ethylenkristallinität von weniger als 35 % aufweist, und
(b) das Plastomer/Elastomer-Blockcopolymergemisch nach einem Folienherstellungsverfahren aus Schlitzdüsenextrusion, Gießdüsenextrusion, Gieß/Präge-Extrusionsverarbeitung oder durch Schmelzblasen des Plastomers in eine Folie umgewandelt wird.

18. Verfahren nach Anspruch 17, bei dem die Folienumwandlung ein Düsengießverfahren ist, bei dem

(a) die Gemischzusammensetzung durch eine Düse mit einem Spalt von mehr als 12,7 x 10^{-3} cm (5 mil) und weniger als 0;304 cm (120 mil) extrudiert wird und
(b) die expandierte Folie rasch abgekühlt wird.

19. Verfahren nach Anspruch 17 oder Anspruch 18, bei dem die Folie über eine Blasfolie oder Gießfoliendüse auf ein gesamtes Abziehverhältnis im Bereich von 2:1 bis 100:1 orientiert wird.

Revendications

1. Film élastomère thermoplastique, comprenant :

   a. 20 à 70 % en poids d'un copolymère séquencé élastomère diène-arène mono-alcénylique comprenant 8 à 55 % en poids d'arène mono-alcénylique
   et b. 30 à 80 % en poids d'un copolymère éthylène/a-oléfine linéaire basse densité, le copolymère ayant une masse volumique comprise dans la plage de 0,86 à 0,900 g/cm^3 (comme déterminé d'après la norme ASTM 1505 conformément à la description), une DPM comprise dans la plage de 2 à 3,5, un indice de fluidité compris dans la plage de 2 dg/min à 1000 dg/min (mesuré d'après la norme ASTM D-1238 190/2.16 et une cristallinité d'éthylène de moins de 35 %.

2. Film suivant la revendication 1, dans lequel le comonomère du copolymère éthylénique comprend une ou plusieurs oléfines à non-saturation éthylénique ayant 3 à 20 atomes de carbone.

3. Film suivant la revendication 2, dans lequel le comonomère comprend un ou plusieurs des monomères propylène, butène-1, hexène-1, octène-1, 4-méthyl-1-pentène et styrène.

4. Film suivant l'une quelconque des revendications précédentes, dans lequel le copolymère a une masse volumique comprise dans la plage de 0,86 à 0,90 g/cm^3.

5. Film suivant l'une quelconque des revendications précédentes, dans lequel le copolymère polyéthylénique a un indice CDBI supérieur à 45 % (mesuré par la technique TREF telle que définie dans la description).

6. Film suivant l'une quelconque des revendications précédentes, dans lequel le copolymère séquencé élastomère est un copolymère styrène-butadiène.

7. Film suivant l'une quelconque des revendications précédentes, dans lequel le copolymère séquencé élastomère est présent en quantités comprises entre 45 % et 65 % en poids.

8. Film suivant l'une quelconque des revendications précédentes, dans lequel le copolymère éthylénique est présent en quantités comprises entre 20 % et 60 % en poids.

9. Film suivant l'une quelconque des revendications précédentes, dans lequel le copolymère élastomère est présent en quantités comprises entre 45 et 65 % en poids et le copolymère d'éthylène est présent en quantités comprises entre 25 et 50 % en poids.

10. Film suivant l'une quelconque des revendications précédentes, dans lequel le copolymère séquencé élastomère est un copolymère styrène-isoprène.

11. Film suivant l'une quelconque des revendications précédentes, dans lequel la déformation permanente (telle que déterminée par la méthode ASTM D-1682 définie dans la description) après un cycle d'allongement de 150 % dans la direction longitudinale ou transversale est inférieure à 40 %.

12. Film suivant l'une quelconque des revendications précédentes, dans lequel la déformation permanente, après un cycle d'allongement de 150 % dans la direction longitudinale ou transversale, se situe entre 5 et 25 %.

13. Film suivant l'une quelconque des revendications précédentes, dans lequel la déformation permanente, après un cycle d'allongement de 300 % dans la direction longitudinale ou transversale, est inférieure à 50 %.

14. Film suivant la revendication 13, dans lequel la déformation permanente est inférieure à 40 %.

15. Film suivant l'une quelconque des revendications précédentes, dans lequel la déformation permanente, après un cycle d'allongement de 200 % dans la direction longitudinale ou transversale, est comprise entre 5 et 15 %.

16. Film suivant l'une quelconque des revendications précédentes, ayant :

   (a) une déformation permanente, après un cycle d'allongem nt d 150 % dans la direction longitudinale ou

transversale, de moins de 20 % ;
(b) une déformation permanente, après un cycle d'allongem nt d 200 % dans la direction transversale, de moins de 25 % ; et
(c) une déformation permanente, après un cycle d'allongem nt d 300 % dans la direction transversale, de moins de 40 %.

17. Procédé de production d'un film élastique, procédé qui comprend les étapes consistant :

(a) à préparer un mélange de 20 à 70 % en poids d'un copolymère séquencé élastomère diène-arène mono-alcénylique, comprenant 8 à 55 % en poids d'arène mono-alcénylique, et de 30 à 80 % en poids d'un copolymère éthylène/α-oléfine linéaire basse densité, le copolymère ayant une masse volumique comprise dans la plage de 0,86 à 0,900 g/cm^3, une DPM comprise dans la plage de 2 à 3,5, un indice de fluidité compris dans la plage de 2 dg/min à 1000 dg/min et une cristallinité d'éthylène inférieure à 35 % ; et
(b) à convertir ce mélange copolymérique séquencé élastomère/plastomère en un film par un procédé de production d'un film par extrusion par une filière droite, extrusion par une filière de coulée, traitement par extrusion avec coulée/gaufrage ou par soufflage du plastomère à l'état fondu.

18. Procédé suivant la revendication 17, dans lequel la transformation en film est un procédé de coulée sous pression qui comprend les étapes consistant :

(a) à extruder la composition de mélange à travers une filière ayant une ouverture supérieure à 12,7x10^{-3} cm (5 in/mil) et inférieure à 0,304 cm (120 in/mil) et
(c) à refroidir rapidement le film en expansion.

19. Procédé suivant la revendication 17 ou la revendication 18, dans lequel le film est orienté à un rapport total de réduction par étirage compris dans la plage de 2:1 à 100:1 par passage dans une filière formant un film soufflé ou un film coulé.

FIG. 1